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PATENT SPECIFICATION

DRAWINGS ATTACHED

895,879



Date of Application and filing Complete Specification: Sept. 15, 1959.

No 31384/59.

Application made in Switzerland on Oct. 30, 1958.

Complete Specification Published: May 9, 1962.

Index at acceptance:—Class 82(2), V2(W:Z1:Z2:Z8), V(3D:4H).

International Classification:—C23c.

COMPLETE SPECIFICATION

Improvements in and relating to the Oxidation and/or Transparency of Thin partly Oxidic Layers

SPECIFICATION NO. 895,879

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of Balzers Patent-Und Lizenz-Anstalt, of Balzers, principality of Liechtenstein, a joint stock company organised and existing under the laws of the principality of Liechtenstein.

THE PATENT OFFICE

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surfaces of bodies, such as precision components of fine mechanisms, of lenses, and of surface mirrors against corrosion and mechanical damage. In the optical industry oxide layers are moreover used as layers of a high or low refractive index for reflection reducing layers, further for interference filters, ray dividers, heat filters, cold light mirrors, or coatings for spectacle lenses. The mechanical and optical properties of such oxide layers depend not only on the kind of oxide applied but to a very large extent also on the kind of method used for applying the same.

The production of oxide layers by direct deposition from the vapour phase of oxidic materials in vacuo and condensation of the vapours on the bases to be coated is well known. This method has for many optical purposes the disadvantage, that most oxides when vaporised and condensed in vacuo produce light-absorbing layers, even when, as the layer-forming material, inherently absorption-free oxides are used. Presumably this is due to the fact that the vacuum has a reducing effect on most oxides at high temperatures, and that—according to a rule valid in general—most unsaturated oxides show optical absorption. There are only a few exceptions from this rule: for example columbium oxide and cerium oxide can be evaporated and absorption-free layers obtained from them.

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of 20 to 30 individual layers, becomes extremely expensive.

The reason is that in the case of the known oxidation of absorbing layers the individual layers are oxidised separately (or at the best only very few individual layers together), since the oxygen diffuses insufficiently through thicker stratified layers. Even with thinner stratified layers the oxidation takes place very sluggishly. Upon subsequent oxidation the layers moreover change their thickness. The keeping of accurate relations of layer thicknesses, which is indispensable for interference systems, is made considerably more difficult thereby. A further disadvantage of this known method consists in that many bodies to which the thin layers are to be applied, e.g. cemented lens systems, must not be heated to the high temperatures required for the oxidation.

The other known method i.e. cathode sputtering in oxygen is inherently very time wasting and leads also to an often non-permissible heating of the bases to be coated. Moreover the layers produced by cathode sputtering often show a stronger light scatter than the layers produced by deposition from the vapour phase from the same layer materials, and therefore are not applicable everywhere.

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Improvements in and relating to the Oxidation and/or Transparency of Thin partly Oxidic Layers

We, GERAETEBAU-ANSTALT, of Balzers in the Principality of Liechtenstein, a joint-stock company organised under the laws of Liechtenstein, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to improving the oxidation and/or transparency of thin partly oxidic layers.

Thin oxide layers have been used in technology to a large extent as protective layers and as layers for optical purposes. As protective layers they serve for protecting sensitive surfaces of bodies, such as precision components of fine mechanisms, of lenses, and of surface mirrors against corrosion and mechanical damage. In the optical industry oxide layers are moreover used as layers of a high or low refractive index for reflection reducing layers, further for interference filters, ray dividers, heat filters, cold light mirrors, or coatings for spectacle lenses. The mechanical and optical properties of such oxide layers depend not only on the kind of oxide applied but to a very large extent also on the kind of method used for applying the same.

The production of oxide layers by direct deposition from the vapour phase of oxidic materials in vacuo and condensation of the vapours on the bases to be coated is well known. This method has for many optical purposes the disadvantage, that most oxides when vaporised and condensed in vacuo produce light-absorbing layers, even when, as the layer-forming material, inherently absorption-free oxides are used. Presumably this is due to the fact that the vacuum has a reducing effect on most oxides at high temperatures, and that—according to a rule valid in general—most unsaturated oxides show optical absorption. There are only a few exceptions from this rule: for example columbium oxide and cerium oxide can be evaporated and absorption-free layers obtained from them.

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In order to overcome these difficulties in the production of absorption-free oxide layers, further methods have been developed. It is known to produce absorption-free metal oxide layers by deposition from the vapour phase of light-absorbent layers and subsequent oxidation thereof, or by cathode sputtering of the metals concerned, in oxygen.

A further known method is deposition from the vapour phase in an oxidising atmosphere.

For the commercial production of thin oxide layers these known methods have the disadvantage of being time-wasting, so that multi-layer systems, for example for heat filters and cold light mirrors (consisting often of 20 to 30 individual layers) become rather expensive.

The reason is that in the case of the known oxidation of absorbing layers the individual layers are oxidised separately (or at the best only very few individual layers together), since the oxygen diffuses insufficiently through thicker stratified layers. Even with thinner stratified layers the oxidation takes place very sluggishly. Upon subsequent oxidation the layers moreover change their thickness. The keeping of accurate relations of layer thicknesses, which is indispensable for interference systems, is made considerably more difficult thereby. A further disadvantage of this known method consists in that many bodies to which the thin layers are to be applied, e.g. cemented lens systems, must not be heated to the high temperatures required for the oxidation.

The other known method i.e. cathode sputtering in oxygen is inherently very time wasting and leads also to an often non-permissible heating of the bases to be coated. Moreover the layers produced by cathode sputtering often show a stronger light scatter than the layers produced by deposition from the vapour phase from the same layer materials, and therefore are not applicable everywhere.

By the best methods hitherto available, for example for the production of a cold light

mirror built up of 25 individual layers of alternately high and low refractive index layers of SiO_2 and TiO_2 such as used e.g. for cinema projectors, about 6 to 8 hours were needed, when the layers had to be hard, well adherent and sufficiently absorption-free.

The present invention relates to a new method for improving the oxidation and/or transparency of thin partly oxidic layers on carriers, wherein a rare earth element and/or a compound of a rare earth element is added to the said layer by cathode sputtering or deposition from the vapour phase in vacuo. The elements of the group of rare earths include yttrium and lanthanum.

According to this method it is possible to produce hard and well adhering oxide layers, with the minimum possible absorption inherent to the layer substances used, in a much shorter time than by the known methods, since in the method according to the invention either no after-oxidation proper in the oxidising atmosphere is necessary or, in case such after-oxidation is necessary the same takes place (in contrast to the known layer-annealing methods) within a short period (often instantaneously). The decomposition from the vapour phase may be carried out at a comparatively high rate. The method according to the invention offers now the possibility of depositing from the vapour phase with a low absorption or free from absorption not only a few oxides which hitherto formed an exception from the general rule, such as cerium oxide, but also other known oxides can now be used for the same purpose, the deposition of which from the vapour phase in vacuo is not per se possible without a reduction thereof taking place.

According to further proposals of the invention the mixing ratio between the layer-forming materials and the admixed elements or compounds from the group of rare earths is so chosen that at least 5% and at the most 50% of all metal atoms contained free or bound in the mixture are cerium atoms or other atoms from the group of rare earths. The admixture of cerium and/or of compounds of cerium or praseodymium and/or the compounds thereof has proved to be particularly effective.

The layers produced by the method according to the invention presumably do not only contain the elements contained in the layer-forming material, such as titanium and silicon, but also the admixed elements or compounds from the group of rare earths as defined hereinabove, which however do not themselves have any disturbing absorption in the visible range.

The invention will be explained with reference to examples. Hard and well adhering layers of high refractive index and practically free from absorption in the visible range of the spectrum are obtained on glass bases, in that a mixture consisting of an oxide of titanium, e.g. TiO_2 , and an oxide of cerium e.g. Ce_2O_3 or Ce_2O_2 are evaporated in the

molecular ratio of 1:1 to 8:1 in vacuo (10^{-5} mm Hg), and deposited on the bases. This mixture evaporates without difficulty in a tungsten crucible at temperatures of 1700° to 2100°C . It is surprising that oxide layers are attained which in the visible range are free from absorption (i.e. according to accepted opinion are saturated with oxygen to a maximum), while the same oxide of titanium in the absence of cerium or of the aforesaid elements or compounds thereof under otherwise equal conditions of deposition from the vacuum yields absorbing layers.

Such an absorption in the visible range occurred hitherto even when the starting material consisted of pure TiO_2 . The effect of the added cerium can possibly be explained in that it promotes the formation of TiO_2 , any oxygen required being supplied by desorption (particularly from the water vapour which is always adsorbed on the wall of the vacuum vessel). The method according to the invention produces absorption-free layers equally by the evaporation of TiO_2 , TiO and (with a short after-oxidation) even of metallic titanium regardless of whether the cerium or the other elements mentioned are admixed in the metallic form or in the form of compounds to the layer-forming material.

Further embodiments, for which the method according to the invention is recommended, are summarised in the accompanying table. The numerical values are stated by way of example only; an expert can easily decide from which of these values he may depart in complying with any particular conditions. As known to a person skilled in the art, for example the evaporating temperature is variable in accordance with the rate of evaporation desired, the latter depending in turn on the refractive index desired of the layer. Quick deposition from the vapour phase generally yields layers of higher refractive index than slow deposition. Obviously also the evaporation period is variable in order to keep a chosen rate of evaporation and/or to attain a desired thickness of the layer. Moreover the gas pressure in the vacuum vessel is variable. Variable in particular are finally the mixing ratios, since there are no sharp limits of the mixing ratio at which the effect aimed at by the invention would make a sudden onset. Accordingly also the properties of the layers obtained vary, but as stated before, the basic discovery of the invention consists in that the optical absorption of the layers obtained by the evaporation and condensation of the mixtures indicated is substantially lower than should have been expected from the mixing ratios only. This finds its expression in that an admixture of more than 5 gram-molecules percent in many of the cases of the examples produced layers practically completely free from absorption, while by simple dilution of the layers obtainable from the layer-forming

materials alone with an absorption-free oxide of the rare earths even at a dilution of 50% half of the original absorption would yet have remained, which usually ranges from the order of magnitude of a few percent to 30% of the incoming light, with a thickness of the layers of $\lambda/4$.

The rule seems to apply that the method according to the invention is suitable particularly for the production of layers of such oxides, the heat of formation of which (related per oxygen atom in the molecule) is smaller than the heat of formation of cerium oxide (CeO_2).

In the following table there are stated:—

In *Section a)* under the numbers 1 to 8 the elements and/or compounds from the group of rare earths which may be admixed to the layer-forming materials. It is often convenient not to use pure elements or compounds from the aforesaid group for admixture to the layer-forming materials, since they are difficult to obtain. On the contrary, the commercial mixtures of rare earths can be used without difficulty, the usual percentage composition of which is indicated in the table. These contents stated in *Section a)* relate to the pure component of the mixture, and are not to be confused with the indication of gram-molecule percentage concerning the addition of the rare earths to the layer-forming materials.

The Table moreover gives examples in *Section b)* namely:—

in line 1: suitable layer-forming materials;
in line 2: commercial rare earth mixtures, which have been proved suitable for the admixture, the indications 1 to 8 meaning that each of the mixtures of substances indicated in section a) may be used;

in line 3: suitable evaporation temperatures for the aforesaid substances;

in line 4: suitable materials for the evaporation crucibles, a distinction being moreover made in the columns 1 and 2, whether oxides or metals had been taken as materials according to line 1. An expert knows also, that many of the substances mentioned may be converted into the

vapour phase by cathode sputtering as well as by thermal evaporation and condensed subsequently on the carriers.

In *Section c)* of the table three different modifications (α , β , γ) of the deposition from the vapour phase are given in the production of layers according to the invention. Thereby the experience known in itself is confirmed, that the deposition from the vapour phase on a carrier at room temperature and in an ordinary vacuum (modification β) may be replaced by deposition from the vapour phase in a higher vacuum but on a carrier at higher temperature (modification α); likewise a shorter period of deposition from the vapour phase (modification γ) requires an after treatment at a somewhat raised temperature.

In *Section d)* the following table finally sets forth examples of modifications according to which the admixture of the elements or compounds from the rare earths is not carried out in one and the same evaporation crucible but in that one or more elements of the group of rare earths and/or one or more compounds of these elements are admixed to a layer previously formed on a carrier by the condensation of a material bringing one or more of the said elements and/or compounds thereof as a thin layer in direct contact with the layer formed from the layer-forming materials, and by subsequently mixing the various substances of the layers by diffusion, preferably by heat treatment.

In *Section d)* metals are indicated which are suitable as layer-forming materials, and the temperatures at which they can be evaporated from carbon crucibles; moreover the metals and compounds suitable for being evaporated from molybdenum crucibles are stated.

The methods according to *Section d)* may alternatively be carried out in such a manner that the layer-forming materials and the elements or compounds from the group of rare earths to be admixed are evaporated at the same time or consecutively in the same vessel from separate vaporisation crucibles, and condensed on the condensation surfaces.

TABLE

| | | | | | | | | | | |
|----|-------------------------|--|---|------------------------|---------|---|---------|-----------|---------|---------|
| a) | 1. Cerium misch metal: | about 50% Ce, 20% Nd, 5% Pr, 25% La and other rare earths | | | | | | | | |
| | 2. Cerium oxide: | 99.9% CeO ₂ | | | | | | | | |
| | 3. Cerite oxide: | about 50% CeO ₂ , 20% La ₂ O ₃ , 5% Pr ₂ O ₃ , 20% Nd ₂ O ₃ , 5% other oxides | | | | | | | | |
| | 4. Lanthanum oxide: | 99.4 La ₂ O ₃ | | | | | | | | |
| | 5. Neodymium oxide: | about 90% Nd ₂ O ₃ , 8% Pr ₆ O ₁₁ , 2% Sm ₂ O ₃ | | | | | | | | |
| | 6. Praseodymium oxide: | about 97% Pr ₆ O ₁₁ , 0.2% Md ₂ O ₃ , 0.25% CeO ₂ , remainder La ₂ O ₃ | | | | | | | | |
| | 7. Samarium oxide: | about 95% Sm ₂ O ₃ , 2% Pr ₂ O ₃ , 1% Nd ₂ O ₃ | | | | | | | | |
| | 8. Didymium oxide: | about 40% Nd ₂ O ₃ , 10% Pr ₂ O ₃ , 13% La ₂ O ₃ , remainder other oxides | | | | | | | | |
| b) | Layer forming material | Si or SiO or Si + SiO ₂ or SiO ₂ | Ti or TiO or Ti + TiO ₂ | Sn or SnO ₂ | Cu | Cr or Cr + Cr ₂ O ₃ or Cr ₂ O ₃ | Mn | Fe or FeO | Ni | Co |
| | Admixture | 1—8 | 1—8 | 1—8 | 1 | 1—8 | 1 | 2—8 | 2—8 | 2—8 |
| | Evaporation temperature | about 1450°C. | 1700° C. | 1350°C. | 1500°C. | 1300°C. | 1050°C. | 1500°C. | 1600°C. | 1800°C. |
| | Material of crucible | for metal mixtures: for oxide mixtures: | for metal C mixtures: for oxide Mo mixtures W | C Mo | Mo | W | Mo | W | W | W |

TABLE—cont.

| c) | Modification | α | β | γ |
|----|--|--------------------------|--------------------------|---------------------------|
| | Deposition period per $\lambda/4$ layer | 2 min. | 2 min. | <imin. |
| | Temperature of | 300° C. | 30° C. | <200° C. |
| | Pressure ($O_2 + H_2O$) | 1×10^{-5} mm Hg | 1×10^{-4} mm Hg | $<5 \times 10^{-5}$ mm Hg |
| | After treatment | nil | nil | annealing 300° C. in air |
| d) | Separate Evaporation of Layer Forming Materials and Elements of Compounds of the Group of Rare Earths (including Yttrium and Lanthanum) from carbon crucibles: | | | |
| | Zr (2100° C.), Th (2400° C.), V (2050° C.) | | | |
| | from molybdenum crucibles: | | | |
| | Pb (800° C.), In (600° C.), Tl (650° C.), ZnO (900° C.), CdO (900° C.), Bi (800° C.), MoO_3 (700° C.), WO_3 (700° C.) | | | |
| | Cerite and Ytria earths (1400° C.) from tungsten crucibles | | | |
| | Mixing ratio of Cerite and Ytria earths: 5 — 50 gram molecule % | | | |

For carrying out the method according to the invention a device according to the accompanying drawing may be used. 1 denotes the vacuum vessel, which may be evacuated by means of a pump through a pipe 2 having a valve 3 to a pressure of 10^{-1} mm Hg or even lower. 4 denotes the vaporisation crucible (sometimes also called a vaporisation boat), wherein the material to be evaporated is fused. This crucible consists of one of the materials indicated in the Table for the vaporisation boat. 5 is the holder device for the crucible, 6 the holder device for the glass plate or lense 7 to be coated from the vapour phase. 8 and 9 are the current leads to the electrical heating coil 10, which surrounds the crucible 4. 11 and 12 form the vacuum-sealed passages for the electrical leads.

The whole arrangement is built-up on a base plate 13. The vacuum-tight sealing between the bell of the vacuum vessel and the base plate is effected by the seal 14.

For many examples of carrying out the method the introduction of oxygen or of water vapour or of atmospheric air into the vacuum vessel is required. For this purpose the gas supply pipe 15 is provided, which may be obturated by means of a valve 16.

For carrying out the method according to the invention in the manner of Section d) of the table two separate crucibles are required in the evaporation appliance. The second crucible may be arranged inside the vacuum vessel in the same manner as the crucible 4, and may be provided with its own current supply leads.

Hereinafter the carrying out of the method according to Section d) of the Table will be explained with reference to a specific example:

In the vacuum evaporation appliance described hereinabove thorium is vaporised from a first crucible of carbon at a temperature of about 2100°C , and the vapours developing are condensed on the lens 7. (Since the crucible consists of carbon, it may be heated by the direct passage of current, without the use of a surrounding heating coil). At the same time from a second crucible arranged in the same vacuum vessel and consisting of tungsten, an element or a compound from the group of rare earths, e.g. the cerium misch-metal mentioned in line a) 1 of the Table is brought to evaporation, the vapours of which condense on the lens simultaneously with the thorium vapours. Accordingly a mixed layer is formed which however is transformed at once under the influence of the elements from the group of rare earths in the presence of oxidising gases into an oxide layer completely free from absorption and consisting partly of thorium oxide, partly of the oxides of the rare earths used. The oxidising gas, e.g. water vapour, is introduced through the pipe 15 by means of the valve 16, up to a pressure in the vacuum vessel of about 2×10^{-1} mm Hg. The amounts

of the materials in the two evaporation crucibles are so chosen that the vapours from the rare earths in the vapour space amount to 5—50 gram molecules percent.

In a slightly modified embodiment of the same method alternately layers of thorium and of cerium misch-metal are applied to the carrier, and these layers are subsequently mixed with one another by thermal diffusion, so that finally a homogenous mixed layer is formed, which oxidises as quickly and readily as if the deposition of the mixture had been effected by evaporation from a common crucible. What has been stated in this example as regards thorium and cerium misch-metal may be applied in an analogous manner also to the other examples from Section d) of the Table.

It has not been discovered what the effect of the method according to the invention is based on, whether possibly on a catalytic effect of the metal from the group of rare earths added pure or in the form of a compound, or perhaps on the formation of specific compounds or intermediate products in the evaporation material and/or in the layer produced. For the technical application it is important that according to this method the periods required for the deposition from the vapour phase of oxide layers known in themselves can be substantially shortened, when it is important to obtain oxide layers of low absorption.

It has often been found convenient in practice to produce the mixtures to be evaporated in a previous melting operation in that a mixture e.g. of Ti, TiO_2 and cerium oxide (or of cerium proper) is fused in vacuo and the solidified product is comminuted and used as a material for the subsequent deposition of thin layers from the vapour phase. In some cases it has however been found convenient in practice to produce the mixtures to be evaporated in a previous sublimation operation; e.g. a mixture of Si and CeO_2 powder is sublimated in vacuo, the product of sublimation is comminuted and used as a starting material for the deposition of thin layers from the vapour phase. When carrying out this method, attention is drawn to the fact that some of the products obtained by sublimation are highly pyrophoric and tend to spontaneous ignition, so that they have to be handled with care and only in small quantities. This has been noted for example with a mixture of SiO and cerium oxide which served for the production of absorption-free silicon oxide layers (SiO alone yields strongly absorbing layers at such layer thicknesses as used for interference systems).

Occasionally it is advantageous to carry out the deposition from the vapour phase while at the same time heating the carrier. The deposition of thin layers from the vapour phase with simultaneous heating of the carrier is already known in itself.

When carrying out the invention an oxida-

tion of the condensate occurs, as stated, the oxygen required being often available even in a vapour phase deposition appliance evacuated to the usual vapour phase deposition vacuum (of 10^{-4} mm Hg or less) in the remaining gas atmosphere to a sufficient extent. Probably the oxygen required is derived, as stated hereinabove, from water vapour desorbed from the walls of the vapour phase deposition appliance.

An artificial enriching in oxygen of the remaining gas atmosphere is often convenient, as has been found, in which case the vacuum and the rate of vapour phase deposition are permissible at a higher magnitude than with the known methods, hard and well adhering layers of the lowest possible absorption being attained nevertheless.

In some cases the complete oxidation of the layers takes place only *after* the deposition from the vapour phase on the carrier, as soon as an oxidising gas mixture (air) is admitted into the vapour phase deposition plant. This subsequent oxidation—a subsequent oxidation of layers being known as such—takes place at a very high rate, when the deposition of the layers has been carried out by the method according to the invention, so that for example, a layer which had been opaque and of metallic lustre is transformed instantaneously into a completely transparent absorption-free oxide layer at the moment of flooding the appliance with atmospheric air and, as the case may be, with the additional effect of moderate heating by the preceding deposition from the vapour phase. Even layer substances, which otherwise could be thoroughly oxidised only by the application of high temperatures and long annealing periods, oxidise readily and quickly, when an element from the rare earths or the compounds thereof has been admixed to the evaporation materials.

We are aware of Patent Specification No. 851,880, the main claim of which is for a method for the production of ultra-violet absorption filters at least partly permeable to light, wherein a starting material containing cerium and/or a cerium compound and at least one further material capable of forming layers permeable to visible light is transformed into the vapour phase by vaporisation in a technical vacuum or by cathodic sputtering, and the vapours thus generated are condensed in a thin layer on a carrier base permeable to visible light, for example of glass, and we do not claim what is claimed in the said Patent Specification No. 851,880.

WHAT WE CLAIM, subject to the foregoing disclaimer, IS:—

1. A method for improving the oxidation and/or transparency of a thin party oxidic layer on a carrier, wherein a rare earth element and/or compound of a rare earth element is added to the said layer by cathode sputtering or deposition from the vapour phase in vacuo.

2. A method according to claim 1, wherein the said rare earth element and/or compound thereof is mixed with the material forming the said layer before being cathode sputtered or vaporised together with it in vacuo.

3. A method according to claim 1, wherein the said rare earth element and/or compound thereof is cathode sputtered or vaporised separately but simultaneously in the same vacuum vessel, and deposited on the said carrier together with the said layer forming material.

4. A method according to claim 1, wherein the said rare earth element and/or compound thereof is cathode sputtered or vaporised in the same vacuum vessel after the cathode sputtering or vaporising of the said layer-forming material and is deposited on the layer formed by the latter on the said carrier.

5. A method according to any of the preceding claims, wherein cerium is the said rare earth element.

6. A method according to any of the claims 1 to 4, wherein praseodymium is the said rare earth element.

7. A method according to any of the preceding claims, wherein the said layer-forming material contains silicon.

8. A method according to any of the preceding claims, wherein the said layer-forming material contains titanium.

9. A method according to any of the preceding claims, wherein the said layer-forming material contains tin.

10. A method according to any of the preceding claims, wherein an oxide of the said rare element is added to the said layer forming material as a source of oxygen for the improved oxidation of the latter.

11. A method according to any of the claims 1 to 9, wherein the oxygen for the oxidation of the said thin layer is derived from the atmosphere in the vacuum vessel, the said rare earth element and/or compound thereof promoting the oxidation of the said layer.

12. A method according to claim 11, wherein the said oxygen is derived from an atmosphere containing free oxygen at a reduced pressure.

13. A method according to claim 11, wherein the said oxygen is derived from traces of water vapour or from traces of water desorbed from the inner wall surface of the said vacuum vessel under a reduced pressure.

14. A method according to claim 11, wherein the said oxygen is derived from atmospheric air flooding the vacuum vessel after the termination of the deposition of the said layer in vacuo.

15. A method according to any of the claims 11 to 14, wherein the said layer and/or its carrier is kept at an elevated temperature.

16. A method according to claim 1, substantially as herein described with reference to any one of the examples.

17. An article having a thin oxidic layer on a carrier when produced by a method according to any of the preceding claims.

S. MITTLER,
Chartered Patent Agent.

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1 SHEET

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